The Dynamic Flammability and Toxicity of Magnesium Hydroxide Filled Intumescent Fire Retardant Polypropylene

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ABSTRACT: The flammability properties of an intumescent fire retardant polypropylene added with magnesium hydroxide was discussed in this study. To evaluate the flammability of the material, limit oxygen index, smoke emission, tensile strength, and our exploitation dynamic flammability evaluation system, tests were assessed in experiments. The results showed that the intumescent flame retardant ammonium polyphosphate-filled polypropylene has superior flammability properties but higher carbon oxide (CO) concentration and smoke density. By adding some magnesium hydroxide additives in intumescent fire retarded polypropylene, the smoke density and CO concentration decrease; and the compound also has superior fire properties. It is concluded that intumescent system and magnesium hydroxide additives are effective on improving combustion properties for polypropylene. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 989–995, 1998

Key words: intumescent; fire retardant; flammability; toxicity; polypropylene

INTRODUCTION

Polypropylene (PP) is used in many applications, for example, in cars, furniture, electronic pieces, electric shells, interior decorations, insulation, architectural material, and so on. However, it has a number of fateful defects, including its emission of smoke and poisonous gas while burning. These drawbacks restrict the range of its field of application. Therefore, it should be an important task to reduce the emission of smoke, poisonous gases, and so on.

In tradition, the halogenated organic compounds were well-known fire retardant additives for PP.[1-2] They were generally used in conjunction with antimony trioxide compounds to enhance their fire retardant efficacy (halogen–metal synergistic effect). On burning, they generally evolve halogen acids and metal halides. However, their proven efficacy as fire retardant is balanced against their known potential effect in increasing the formation of toxic gases and corrosive smokes. It had recently been reported that some currently used brominated aromatic fire retardant may form highly toxic brominated dibenzodioxines and dibenzofurans while burning.[3-4] In the search for halogen-free fire retardant, there is increasing attention on the intumescent and metallic hydroxide fillers.

The intumescent fire retardant, while burning, gives a swollen multicellular char, which protects the underlying material from the action of the fire. This approach was derived from coating for the protection of structures. The coating material is an incorporation of intumescent additives in polymeric material. This method had been used for more than 40 years.[5] The mechanism of fire retardant is assumed that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the mate-

Table I   The Compositions of PP-FR Resins

	PP	PMA₀₀	PMA₁₀	PMA₃₀	PMA₅₀	PMA₇₀
PP (phr)	100	100	100	100	100	100
APP (phr)	—	23	23	23	23	23
PE (phr)	—	14	14	14	14	14
Melamine (phr)	—	13	13	13	13	13
Mg(OH)₂ (phr)	—	—	10	30	50	70

rial to volatile combustible products.[6-7] Ammonium polyphosphate (APP) is most used as the acid source in intumescent systems. While heating, its forming polyphosphoric acid is a well-known acid catalyst for organic reactions.

In metallic hydroxide fillers, the magnesium hydroxide [Mg(OH)₂] is a considerable acid- and halogen-free fire retardant additive for polymers,[8] which has a smoke-suppressing capability. The effectiveness of this widely used fire retardant depends on the following factors.[9-10]

1. The endothermic decomposition release water of hydration from the substrate retards the rate of thermal degradation.
2. The accompanying release of inert gases (water vapor) dilutes the fuel supply present in the gas phase.
3. The relatively higher heat capacity of the fire retardant reduces the thermal energy available to degrade the substrate.
4. The decomposition products may insulate the substrate from the heat source.

Its temperature of decomposition is near 350°C, making certain its incorporation with a wide-range of polymers, including PP.[11]

According to the above analysis, the intumescent additives and Mg(OH)₂ were adopted as the fire retardant for PP in this study. In the experiment, we prefer that the test device should be able to simulate the properties of the burned material in an atmosphere environment. It should also be able to analyze the physical and chemical effects invoked by the burning. However, the older test methods almost invariably supply a qualitative pass–fail output. They are of little use in the

study of the material combustion's mechanism, which is important for the development of fire retardant materials. Therefore we referred to ISO 5660[12] and ASTM-E-1354[13] and developed a combustion evaluation machine, which is named the "dynamic flammability evaluation system".[14] This system can record mass loss rate, heat release rate, toxic gases, and other combustion properties in real time. The heat release rate (HRR) during combustion is generally considered to be one of the most important parameters for characterizing the combustion behavior of organic materials. On the other hand, the limit oxygen index (LOI), smoke emission properties, and mechanical properties are also evaluated in this study by experiment.

EXPERIMENT

Materials

The following products were used in the experiment: Isotactic polypropylene (PP, Pro-Fax 366); hydroxide magnesium [Mg(OH)₂]; Star Brand 100, 90% < 0.85 μm); ammonium polyphosphate (APP, 90% < 0.6 μm); pentarythriol (PE, 90% < 1 μm); melamine (ME, 90% < 0.5 μm).

These fillers are added to PP by mixing in a Brabender at 200°C. Specimens for traditional combustion test (LOI, smoke density) and slabs (100 × 100 mm², 3 mm thick) for burning in the dynamic flammability evaluation system were prepared by hot pressing at 100 kg/cm² at 200°C. The various samples made from PP and fire retardant are given in Table I, where parts per hundred parts of resin (phr) is the unit often used

Table II   The Limit Oxygen Index of PP-FR Resins

	PP	PMA₀₀	PMA₁₀	PMA₃₀	PMA₅₀	PMA₇₀
LOI	17.8	34.5	25.2	28	28.8	30.2

Table III   The Dynamic Flammability Parameters of PP-FR Resins

Material	Heat Flux (kW/m²)	TTI (s)	BP (%)	MLR (g/s)	Maximum HRR (kW/m²)	Average HRR (kW/m²)	THR (MJ/m²)	EHC (MJ/kg)	Flash-Over Index
PP	50	24	100	0.0617	687	284	119	45	0.0349
PMA_{00}	50	36	94.2	0.0244	115	70.6	67.8	28.8	0.313
PMA_{10}	50	36	90.8	0.0303	156	87	63.9	29.1	0.231
PMA_{30}	50	43	80.4	0.0238	121	69	58.2	28.4	0.355
PMA_{50}	50	43	77	0.0228	121	65.3	54.5	28.6	0.355
PMA_{70}	50	44	71.3	0.0198	104	57.5	53.6	28.9	0.423
PP	25	166	100	0.0321	412	135	105	42.1	0.403
PMA_{00}	25	188	81.2	0.0109	65	24.9	46.3	22.9	2.892
PMA_{10}	25	196	84	0.0129	79.5	27.8	45.1	21.9	2.46
PMA_{30}	25	217	74.2	0.0138	68.8	29.8	39.3	21.6	3.15
PMA_{50}	25	220	70.9	0.0135	57.3	27.6	36.4	20.4	3.83
PMA_{70}	25	232	63.8	0.0121	54.3	23.1	31.2	19.1	4.27

in industry.[16] For example, PP 100 phr with fire retardant 30 phr means 100 g PP mixed with 30 g of fire retardant additives.

Test

Dynamic Flammability Evaluation System

The dynamic flammability evaluation system was operated following the procedure defined in ISO 5660 under heat fluxes of 25 and 50/kW m². This system can measure the flammability properties shown as follows.

- Time to ignition (TTI [s]): The time until the entire surface of the sample burns with a sustained luminous flame.
- Burning percentage (BP): the percentage of the mass lost during burn.
- Mass loss rate (MLR [g/s]): the ratio of the total mass loss over the total burning time.
- Heat release rate (HRR [kW/m²]): an instantaneous amount of heat release from material per surface area.
- Effective heat combustion (EHC [kJ/g]): the ratio of the total heat release over the total mass lost.
- Flash-over index (FOI): the ratio of TTI and maximum HRR.
- Carbon oxide (CO) concentration (CO [ppm]): the instantaneous concentration of CO during burning.

Limit Oxygen Index

The minimum oxygen concentration required to sustain burning was measured on a specimen (120 × 6 mm², 3 mm thick) held vertically in a Polymer Laboratory System HFTA II instrument referred to ASTM-D-2863.

Smoke Emission Properties

Smoke evolution properties were determined by using a smoke chamber conforming to National Bureau of Standards specifications in smoldering conditions. This experiment was proceeded on a specimen (75 × 75 mm², 3 mm thick) in a Polymer Laboratory System SN-2400 instrument following ASTM-E-662 specification. Its results are reported in terms of the specific optical density as function of time.

Mechanical Properties

The tensile strength experiment was performed by ASTM D638 Type IV Material Test System (Corp. model MTS 810). The elongation rate was set at 20 mm min.

RESULT AND DISCUSSION

Combustion Properties

Limit Oxygen Index

The LOI of PP and fire retarded PP are listed in Table II. It can be seen that the LOI value of pure PP is very low (17.8). It means that PP is

flammable. By adding APP in pure PP, the LOI value of PMA_{00} is 34.5 and shows good protection for PP. This is because of the intumescent fire retardant interrupts burning by condensed phase. However, if 10 phr $Mg(OH)_2$ is added, PMA_{10} shows a considerable decrease of the LOI value. It is evident that APP has better efficacy in flame retardancy than $Mg(OH)_2$; but if more $Mg(OH)_2$ is added, the LOI value will raise again.

Dynamic Flammability

All parameters of dynamic flammability are listed in Table III. Lower BP, MLR, maximum HRR, average HRR, THR, EHC, and higher TTI, flash-over index values indicate less fire hazard. The HRR during combustion is generally considered to be one of the most important parameters for characterizing the combustion behavior of organic materials. In this study, instantaneous HRR is calculated using the oxygen consumption principle.[16] The HRR curves of various samples under heat flux of 50 and 25 kW/m^2 are shown in Figures 1 and 2.

Table III indicates that pure PP has low resistance to combustion. With an addition of intumescent fire retardant, the maximum HRR of PMA_{00} under heat flux of 50 kW/m^2 decreases from 687 to 115 kW/m^2; and the THR and EHC also decrease markedly. It is because, while burning, a foamed multicellular char on the surface of the material makes a thermal insulation and provokes the extinguishment of the flame. It prevents combustible gases from feeding the flame and also separates oxygen from the burning material. When the material absorbs more heat, the carbonaceous char will break, and some heat will be released. The new carbonaceous char will generate immediately, and the phenomenon will occur repetitively. Therefore, the material decomposes in many steps on burning. It can be seen some steps in the heat release curves. Also, it is shown that PMA_{10} is getting worse than PMA_{00} in HRR. However, some flammability properties are superexcellent in $Mg(OH)_2$-filled PP. The combustion properties will be improved if more $Mg(OH)_2$ is added.

One of the characteristics of the dynamic flammability evaluation system is the measurement of the MLR (mass loss rate) and the BP (burning percentage) during the combustion test, which allows a mechanistic insight in the combustion process. By the addition of intumescent fire retardant in pure polyphosphate, under heat flux 50 kW/m^2, the BP decreases from 100% (PP) to
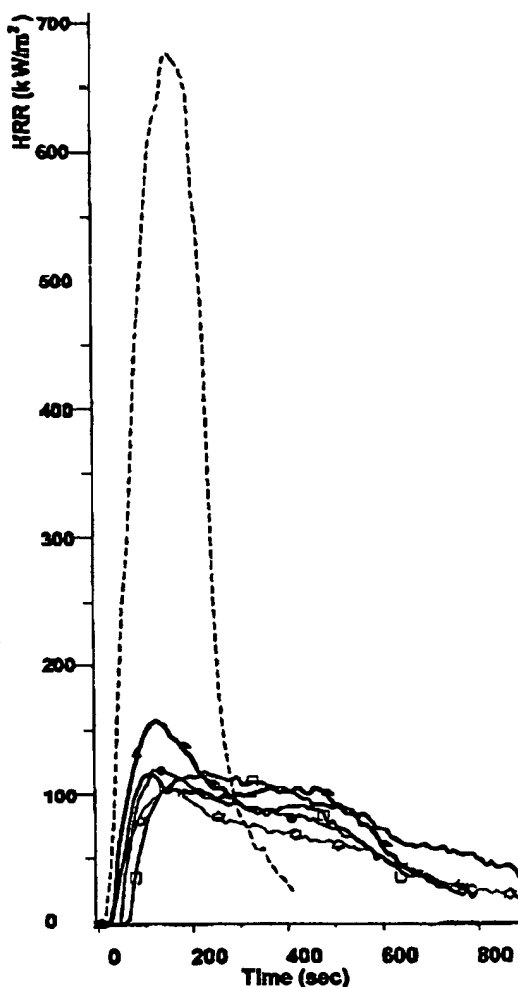

Figure 1   HRR versus time curve for PP-FR resin (50 kW/m^2): (----) PP, (—) PMA_{00}, (▲) PMA_{10}, (□) PMA_{30}, (●) PMA_{50}, and (○) PMA_{70}.

94.2% (PMA_{00}); and the MLR also decreases from 0.0617 to 0.0244 g/s. On the other hand, with the increase of the $Mg(OH)_2$, the BP will conspicuously decrease; but the MLR will raise and then drop. It is evident that intumescent fire retardant is more effective than the $Mg(OH)_2$ on retarding material combustion.

FOI (flash-over index) may be the best individual indicator of overall fire hazard. From Table III, the FOI will arise, and the TTI (time to ignition) will be elongated. It is concluded that the
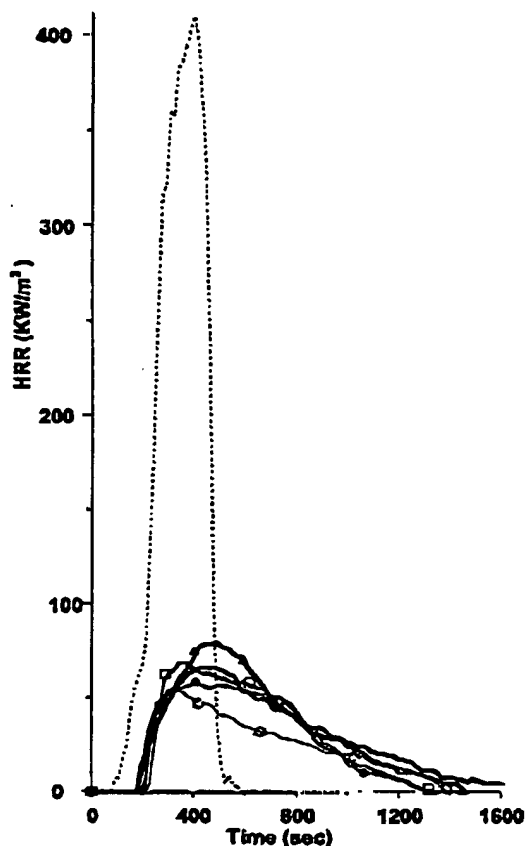
Figure 3   CO concentration versus time curve for PP–FR resins (50 kW/m²): (----) PP, (—) PMA₀₀, (▲) PMA₁₀, (□) PMA₃₀, (●) PMA₅₀, and (✿) PMA₇₀.

Figure 2   HRR versus time curve for PP–FR resin (25 kW/m²): (----) PP, (—) PMA₀₀, (▲) PMA₁₀, (□) PMA₃₀, (●) PMA₅₀, and (✿) PMA₇₀.

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fire retardant is effective in improving the flammability properties of PP.

Toxicity

CO Concentration

The CO Concentration versus time chart for pure and fire retardant PP is shown in Figure 3 (under a heat flux of 50 kW/m²) and Figure 4 (under a heat flux of 25 kW/m²), and Table IV lists the maximum and average values of CO concentration. It is evident that the pure PP has much higher CO concentration than fire retardant PP, and the CO versus time curve of pure PP has a single peak only. With the retardant addition, the CO curve from a single peak increases to many
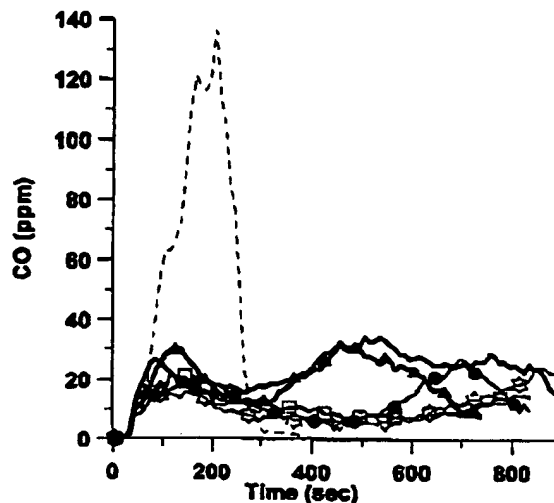

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Table IV   The Toxicity and Tensile Strength of PP-FR Resins

Material	Heat Flux (kW/m^2)	Maximum CO (ppm)	Average CO (ppm)	Maximum Smoke Density (D_m)	Time to $D_s = 16$ (min)	Strength (Pa)
PP	50	143	41.6	822	2.13	20.91
PMA$_{00}$	50	35.2	20.4	528	2.63	13.98
PMA$_{10}$	50	33.3	19.1	526	2.7	13.45
PMA$_{30}$	50	22.3	11.2	478	2.86	12.76
PMA$_{50}$	50	27.6	11.6	453	2.93	11.50
PMA$_{70}$	50	25.4	10.7	436	3.36	10.84
PP	25	63.2	17.9	—	—	—
PMA$_{00}$	25	14.5	9.64	—	—	—
PMA$_{10}$	25	12.3	12.3	—	—	—
PMA$_{30}$	25	14.5	14.5	—	—	—
PMA$_{50}$	25	19.3	19.3	—	—	—
PMA$_{70}$	25	22.1	22.1	—	—	—

Smoke Emission Properties

The specific optical density of smoke (D_s) experiments were done under smoldering test conditions. The results are shown in Figure 5 and Table IV. From these results, it can be seen that PP is a high-smoke polymer (maximum D_s = 822). Experiments showed that retardant additives not only reduce the overall level of smoke generated but also delay the onset of detection smoke. It is concluded that increasing the amount of

Figure 5   Specific optical density of smoke versus time curve for PP/FR resins: (----) PP, (—) PMA$_{00}$, (▲) PMA$_{10}$, (□) PMA$_{30}$, (●) PMA$_{50}$, and (✧) PMA$_{70}$.

Mg(OH)$_2$ can reduce the overall level of smoke generated. This is because the metallic hydroxide reacts with decomposed hydrocarbon species.

Mechanical Properties

Table IV lists the results of tensile strength tests. It is evident that adding too much filler to PP will effect its inherent superior mechanical property. If we add 70 phr Mg(OH)$_2$ to intumescent fire retardant PP (PMA$_{70}$), the tensile strength will decrease approximately 49%, from 20.91 to 10.84 Pa.
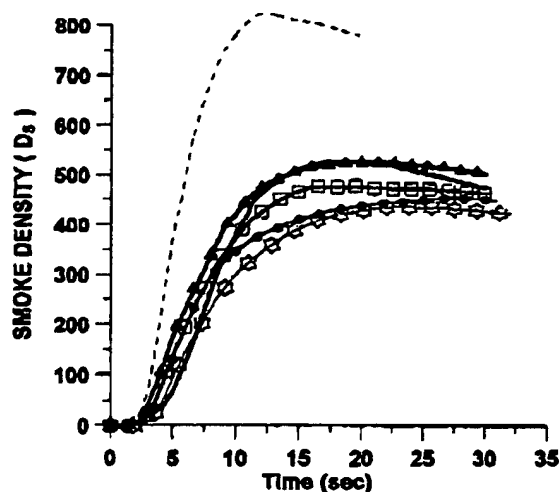
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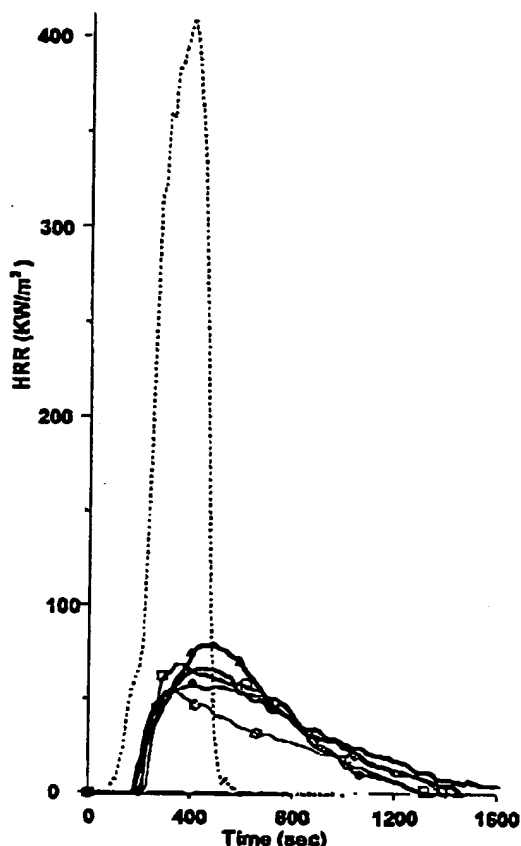
Figure 2   HRR versus time curve for PP–FR rosin (25 kW/m^2): (----) PP, (—) PMA$_{00}$, (▲) PMA$_{10}$. (□) PMA$_{30}$, (●) PMA$_{60}$, and (○) PMA$_{70}$.

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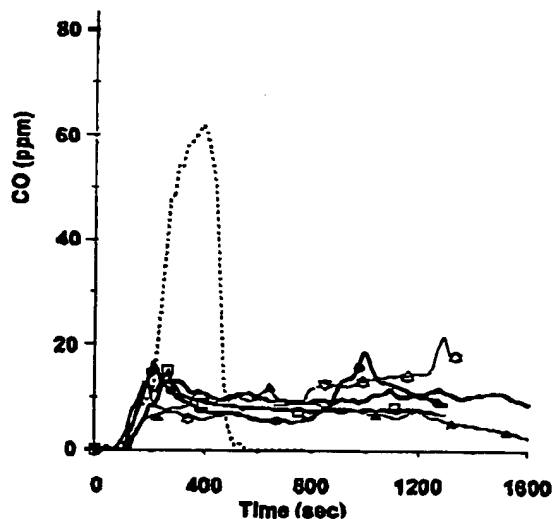Figure 4   CO concentration versus time curve for PP–FR resins (25 kW/m^2): (----) PP, (—) PMA$_{00}$, (▲) PMA$_{10}$, (□) PMA$_{30}$, (●) PMA$_{60}$, and (○) PMA$_{70}$.

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PMA_{50}	50	27.6	11.6	453	2.93	11.50
PMA_{70}	50	25.4	10.7	436	3.36	10.84
PP	25	63.2	17.9	—	—	—
PMA_{00}	25	14.5	9.64	—	—	—
PMA_{10}	25	12.3	12.3	—	—	—
PMA_{30}	25	14.5	14.5	—	—	—
PMA_{50}	25	19.3	19.3	—	—	—
PMA_{70}	25	22.1	22.1	—	—	—

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NOMENCLATURES

FR   fire retardant
TTI   time to ignition
BP   burning percentage
MLR   mass loss rate
HRR   heat release rate
THR   total heat release rate
EHC   effective heat combustion
FOI   flash-over index
LOI   limit oxygen index
D_s specific optical density of smoke
D_m maximum specific optical density of smoke

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Effect of Fillers on Fire Retardancy of Intumescent Polypropylene Blends

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Summary: Addition of Ammonium Polyphosphate/Polyamide-6 system is known to provide flame retardancy in many polymers blends via an intumescent process. Particulate fillers (talc and calcium carbonate) are used in large quantities in PP. Combination of fillers in PP can modify the properties of the polymeric matrix. This study investigates the effect of fillers (talc and calcium carbonate) on the fire performance of the Polypropylene/Ammonium polyphosphate/Polyamide-6 blend. It is shown that the fire performance strongly depends on the nature of the filler used. Talc increases and calcium carbonate decreases in the fire performance of the blend.

Keywords: ammonium polyphosphate, cone calorimetry, intumescence, polyamide-6, polypropylene, talc and CaCO$_3$

Introduction

Polypropylene (PP) is representing a big part of polymer worldwide consumption just after polyvinyl chloride and polyethylene. Addition of low cost fillers such as calcium carbonate or talc, was historically justified by cost reduction but more and more improvement of performance becomes the main driver. The low cost material have numerous advantages like a high modulus, excellent chemical resistance and easy process conversion. This explains why the polymer has grow significantly in automotive or appliances.[1]

Moreover, for safety reasons, applications of polyolefinic materials in common transport, materials require fire retardant properties. One way to increase the fire properties is to develop intumescent systems.

Intumescent technology[2],[3] has found a place in polymer science as a method of providing flame retardancy to polymeric materials.[4],[5] On heating, fire retardant (FR) intumescent materials form a foamed cellular charred layer on their surfaces, which protects the underlying materials from the action of heat flux and flame. The proposed mechanism is based on the

charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phase.[6] Generally, intumescent formulations contain three ingredients: an acidic source, a carbonisation agent and a blowing agent.

It was shown that incorporating ammonium polyphosphate (APP) in polyamide 6 (PA-6) provides fire properties of interest.[7]-[8] However, the compatibility of the APP/PA6 blends obtained by direct mixing of APP in melted PA-6, is low : a migration of the mineral salt [9] occurs during solidification of the melt. In this case, the use of an interfacial agent is required. Ethylene-vinyl-acetate (EVA) copolymers, which are known to be very efficient interfacial agents[10]-[11] have thus been used as compatibilisers in the intumescent PP/APP/PA6 system. That has been revealed using calorimetry by oxygen consumption that fire properties of interest were obtained by using EVA_{24} as interfacial agent in the PP/APP/PA-6 intumescent system.[12] Moreover, some authors have shown that fillers, particularly glass fibres, have a great influence on the fire properties and lead to an increase in the fire performance.[13]

In this study, the effect of talc and calcium carbonate on the fire properties are investigated and compared with the PP/PA-6/APP/EVA_{24} system without fillers.

Experimental

Materials

Raw materials were polypropylene (homopolymer grade 3120 MN 1 MFI 8 (230°C, 2.16kg), as pellets supplied by Appryl), PA-6 (as pellets supplied by Nyltech), APP (AP 462: $(NH_4PO_3)_n$, n ≈ 700, powder supplied by Clariant), EVA_{24} supplied as pellets by Elf-Atochem (EVATANE grades). Polypropylene talc (PPTALC, MFI Polyfort FPP 20 T as pellets supplied by Schulman S.A. hereafter called talcom).

Two fillers were added into the polypropylene : Talc (mean size of particles 15 μm supplied by Suommen takki) and Calcium carbonate (mean size particles 2.5 μm supplied by Omnia).

Processing and Formulations

The fillers (talc and $CaCO_3$ without sizing agent) were added to PP using a Brabender DSK 42/7 intermeshing counter-rotating twin-screw extruder at 190°C and 150 rpm to obtain a composite with mineral loading of 20 wt-%. Then the PP composites were mixed with PA-6, APP, and EVA_{24} using a Brabender Mixer measuring head (type 350/EH, roller blades) at 230°C and 50 rpm. We have checked the mixing conditions using the data processing torque rheometer system Brabender Plasticorder PL2000. Sheets (100 x 100 x 3 mm³) were then

obtained using a Darragon pressing machine at 200°C and at a pressure of 10^6 Pa. The different processed blends mixed are listed in Table 1.

Table 1. Composition of the PP based blends.

PP (wt-%)	PA-6 (wt-%)	APP (wt-%)	Talc (wt-%)	CaCO₃ (wt-%)	EVA₂₄ (wt-%)	Samples label
60	8.75	26.25			5	Reference
48	8.75	26.25	12		5	PPtalcom
48	8.75	26.25	12		5	PPtalc
48	8.75	26.25		12	5	PPcarb

Fire Testing

Limiting Oxygen Index (LOI) was measured using a Stanton Redcroft instrument on sheets ($100 \times 10 \times 3$ mm³) according to ASTM 2863.[14] UL-94 tests were carried out on $127 \times 12.7 \times 3$ mm³ sheets according to the UL-94 testing.[15]

Samples are exposed to a Stanton Redcroft Cone Calorimeter according to ASTM 1356-90 and ISO 5660 at an external heat flux of 50 kW/m² which corresponds to the heat evolved during a fire.[16] Conventional data (Rate Heat Release (R.H.R.), Total Heat Emitted (T.H.E.), CO/CO₂ evolutions and residual mass) were computed using a software developed in our laboratory. For experiments performed at 50 kW/m², RHR and THE values were reproducible to within ±10% and weight loss, CO, CO₂ were reproducible to within ±15%. The data presented in the following are averages from at least 3 experiments.

Thermal Analysis

Thermogravimetric analyses were carried out at heating rate 10°C/min in a flowing synthetic air (Air Liquid grade; flow rate = 5.10^{-7} Nm³/s) using a SETARAM MTB 10-8 thermobalance. In each case, samples were 10 mg and were positioned in open vitrous silica pans. The precision on temperature measurements is ± 1.5°C in the range 50°C-850°C.

The curves of weight difference between the experimental and theoretical TG curves are computed as follows : $\Delta(T)$: curve of weight difference : $\Delta(T) = M_{exp}(T) - M_{th}(T)$. with:

$M_{th}(T) = (0.60-X)M_{poly}(T) + XM_{fill}(T) + 0.2625M_{APP}(T) + 0.0875M_{PA-6}(T) + 0.05M_{EVA}(T)$.

Where $M_{poly}(T)$, $M_{APP}(T)$, $M_{PA-6}(T)$, $M_{fill}(T)$, $M_{EVA}(T)$ and $M_{exp}(T)$ are respectively the polymer weight, APP, PA-6, the fillers and of the blends given by their TG curves.

The $\Delta(T)$ curves allow to point out an eventual increase or decrease in the thermal stability of the polymeric matrix related to the presence of one or every additives.[17]

Results

Fire Testing

LOI values and UL-94 rating of the different blends are given in the Table 2.

Table 2. LOI values and UL-94 ratings of the intumescent blends versus the fillers grade.

Blends	LOI (vol %)	UL-94 rating
PP/PA-6/APP/EVA$_{24}$	32	V0
PPcarb/PA-6/APP/EVA$_{24}$	29	V1
PPtalc/PA-6/APP/EVA$_{24}$	31	V0
PPtalcom/PA-6/APP/EVA$_{24}$	32	V0

Incorporating talc has no effect on the LOI nor on the UL-94 rating whereas with $CaCO_3$, the LOI value is lower than those obtained with talc or without fillers. Moreover, a V1 rating is obtained with $CaCO_3$ whereas a V0 rating is achieved with the other formulations. Using $CaCO_3$ leads to a decrease of the fire performance of the blend.

The R.H.R. curves of the formulations are presented on Fig. 1.

Incorporating APP with PA6[12] in PP and PP/fillers blends leads to the development of an intumescent structure in the cone calorimeter conditions. Whatever the blend, two peaks are observed separated by a plateau value of R.H.R. According to other studies,[6] the first peak may be assigned to the development of the intumescent protective structure. The formation of a stable efficient protective shield may explain the plateau value where the R.H.R is roughly constant. The second peak is assigned to the degradation of this protective layer.

Incorporating calcium carbonate in the blend increases the first RHR peak from 200 kW/m² without fillers to 350 kW/m² and decreases the time needed for the complete degradation of the polymeric material.

Adding talc decreases the first peak of RHR but no significant difference of the time to destruction and of the second RHR peak value is observed. However, it seems that the best results are obtained using the commercial PPtalc matrix. The stability of the shield is about 420 seconds whereas it is 350 seconds for the other blends.
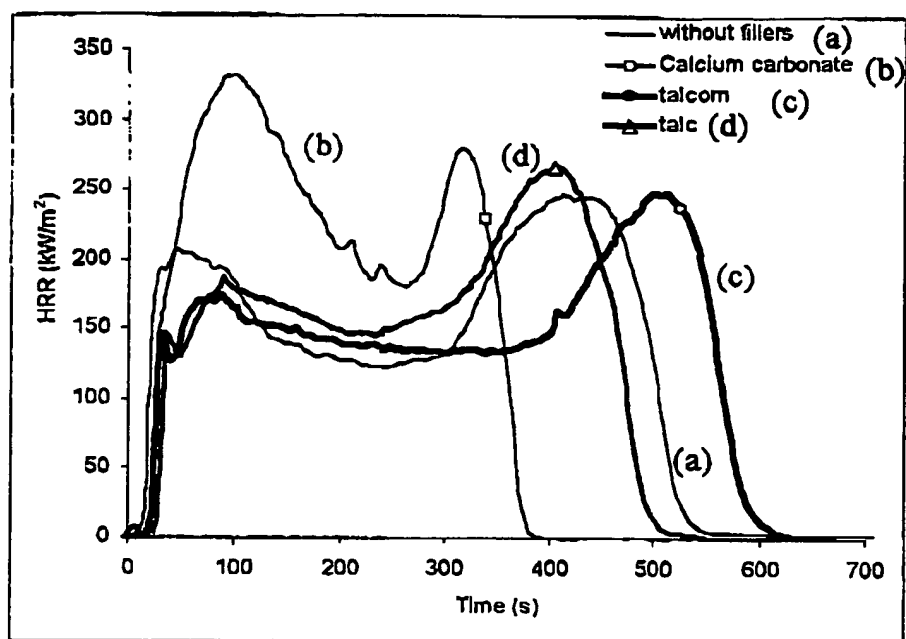
Fig. 1. R.H.R. versus time for PP/APP/PA6/EVA₂₄ formulations at an heat flux of 50 kW/m².

The curve of the total heat evolved during the test are plotted on Fig. 2.
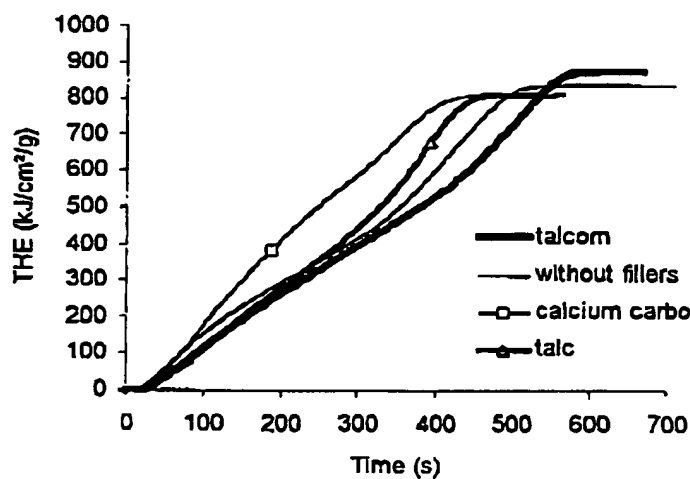
Fig. 2. THE versus time for PPfillers/APP/PA6/EVA₂₄ formulations at an external heat flux of 50 kW/m².

Incorporating fillers does not lead to a decrease in the final THE value. However, the time to heat release depends upon the fillers and is highly decreased using $CaCO_3$. The final THE is the same whatever the blend.

CO_2 and CO emissions curves are plotted on Fig. 3 and Fig. 4.
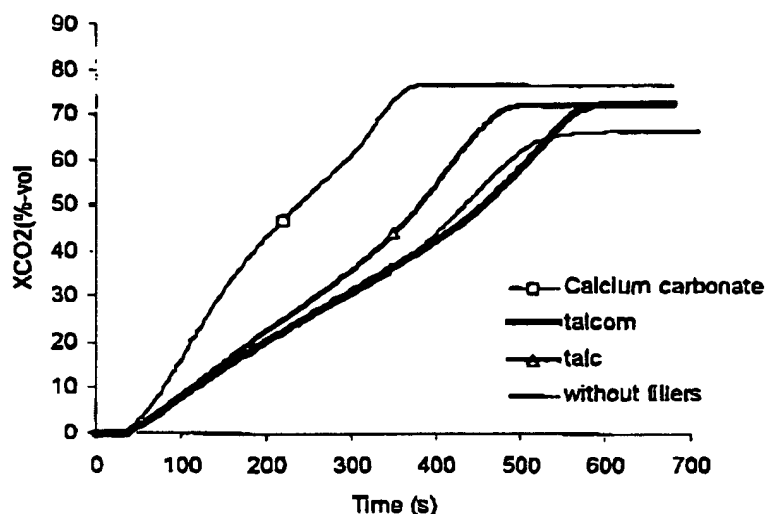
Fig. 3. CO_2 emission versus time for $PP/APP/PA6/EVA_{24}$ formulations under an external heat flux of 50 kW/m^2.
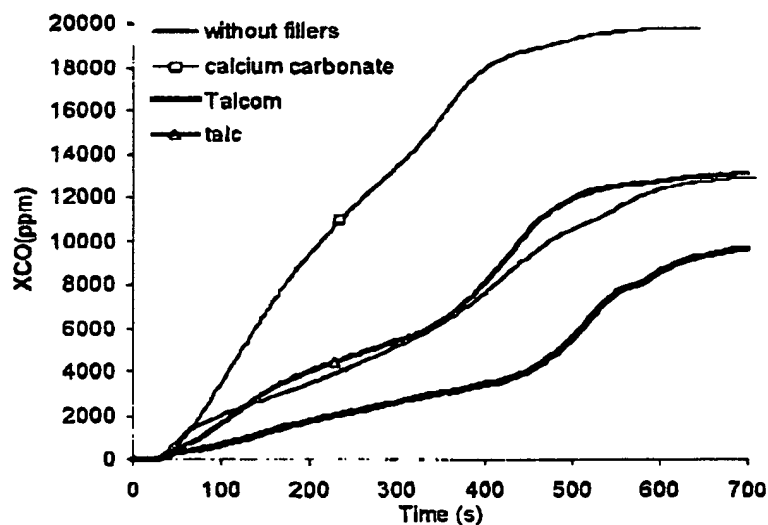
Fig. 4. CO emission versus time for $PP/APP/PA6/EVA_{24}$ formulations under an external heat flux of 50 kW/m^2.

Incorporating fillers lead to an increase in the final among of evolved CO_2. Adding talc allows to increase the delay of the CO and CO_2 emission compared to the blend with $CaCO_3$. This delay particularly increases with the commercial product and the amount of CO evolved decreases. Moreover, the amount of CO_2 evolved does not increase. So, a part of the carbonaceous residue is preserved. Nevertheless, the efficiency of talc is reduced when the blend extruded in our lab is considered. Using $CaCO_3$ induces a decrease in the delay to obtain the maximum value. This could be interpreted as a destabilisation of the protective shield.

An increase in the amount of the evolved CO for the blend with $CaCO_3$ is noted Fig. 4, compared to the other blend. This is probably due to the degradation of $CaCO_3$. This hypothesis will be discussed in the following.

The residual weight curves for the blends versus time are plotted on Fig. 5.
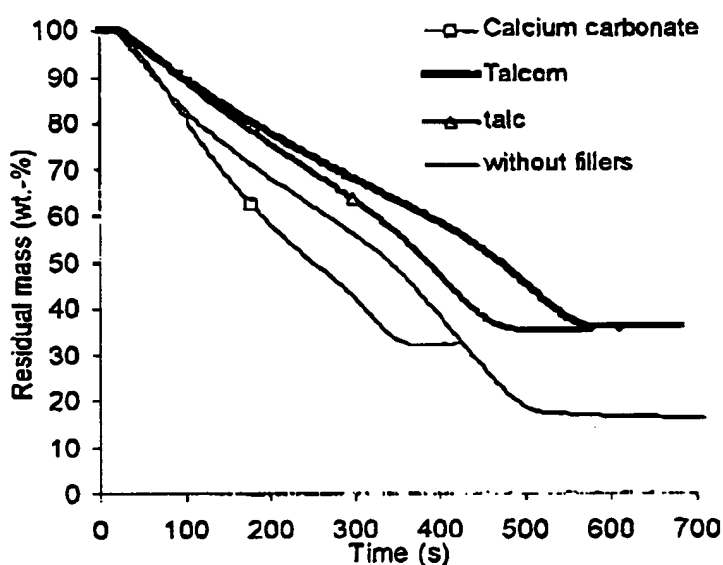
Fig. 5. Evolution of the residual mass for PP/APP/PA6/EVA$_{24}$ formulations versus time under an heat flux of 50 kW/m^2.

Incorporating talc enables to obtain a final residual weight greater than without. Moreover, as previously observed, using talc enables to get a higher stability of the material which is maximal using the commercial product.

Using $CaCO_3$ leads to a loss of the thermal/fire stability in the cone calorimeter condition. The amount of residual weight obtained is about 35 wt-% with talc and 30 wt-% with calcium carbonate whereas it is only 17 wt-% without. As there is 13 wt-% of fillers, with talc in the cone calorimeter conditions, some materials are preserved.

The curves of the thermo-oxidative degradation of the blends with their fillers and their derivatives are plotted Figure 6 and Figure 7.

Fig. 6. TG curves under air of the PP/APP/PA-6/EVA$_{24}$ intumescent blend (heating rate: 10°C/min).

Fig. 7. DTG curves under air of the PP/APP/PA-6/EVA$_{24}$ intumescent blend (heating rate: 10°C/min).

TG and DTG curves of the PP/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) show four significant changes in the slopes, which prove that its degradations is at least a four main steps process. Previous studies show that the carbonization process of the system occurs via 4 steps.[17] From 230°C the additives react and form phosphate esters. Between 280°C and 350°C, the development of intumescence occurs and between 350°C and 430°C, the intumescent coating degrades. At higher temperatures, there are structural changes leading to the formation of a new carbonaceous species (established in the temperature range 430°C < T < 560°C) up to 430°C which may be interpreted as above. Then a plateau is observed between 430-560°C. This plateau may be assigned to a particular protective "carbon". Finally, the curve decreases at higher temperature. There is modification of the carbonaceous structure which is no longer protective and the formation of a "high temperature" residue (about 4 wt.-% at 800°C).

TG and DTG curves of the PPtalc/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) are similar to the curves of the blend without fillers until 560°C. Beyond 560 °C, a high temperature residue (about 32 wt-%) is obtained.

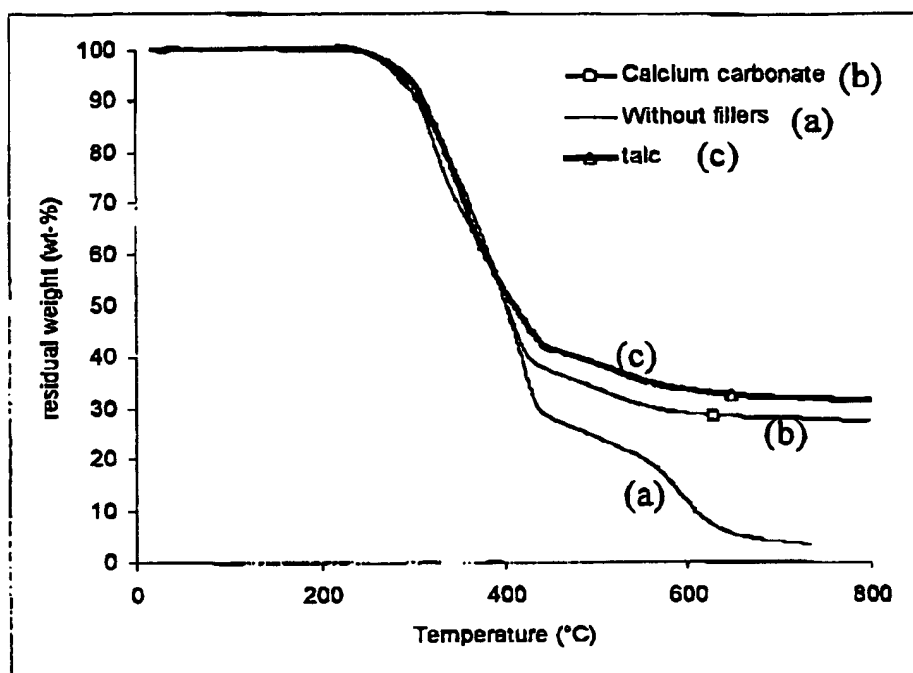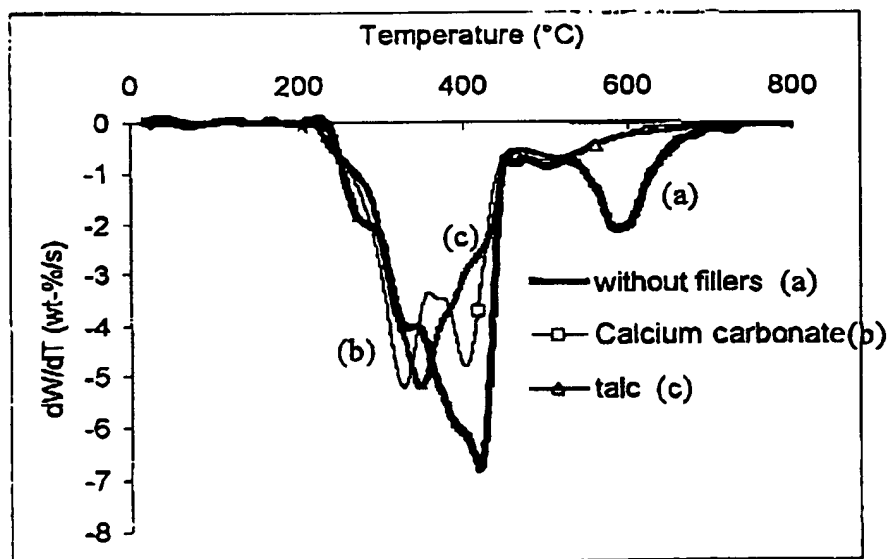TG and DTG curves of the PPcarb/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) shows three significant changes in the slopes, which prove that its degradations is at least a three steps process. The first one begins at about 250°C until 430°C. Then, the material shows a low rate degradation between 430°C and 560°C, and finally a high temperature residue (about 28 wt-%) is formed.

The ΔT curves are presented Figure 8. Under the conditions of thermo-oxidative degradation, it is observed that the protection by the intumescence phenomenon is a several steps' process.

In the case of PP/PA-6/APP/EVA$_{24}$, the curve of weight loss difference shows that interactions between the additive and the polymeric matrix occur. The formation of the intumescent coating occurs from 210°C which implies a comparatively more important stability of the system (experimental curve>simulated curve) from 350°C up to 500°C. In this region (210<T<500°C), a first coating is formed with a maximum of protection at 380°C. Above this temperature, the shield looses partially its efficiency. Above 420°C, a second protective process is observed which leads to the formation of a second shield. This latter acts as a relay of the first one. Finally from 560°C, we can assume degradation of the material (fast decrease of weight difference) and the formation of a residue.

In the case of PP/talc/PA-6/APP/EVA$_{24}$, the curve of mass difference has the same shape as PP/PA-6/APP/EVA$_{24}$ up to 450°C which may be interpreted as above. Then a plateau is observed between 450-550°C. This plateau may be assigned to a particular protective "carbon".

Finally the curve increases until 630°C, a second protective process is observed which leads to the formation of a second shield. Then a plateau is observed at high temperature.
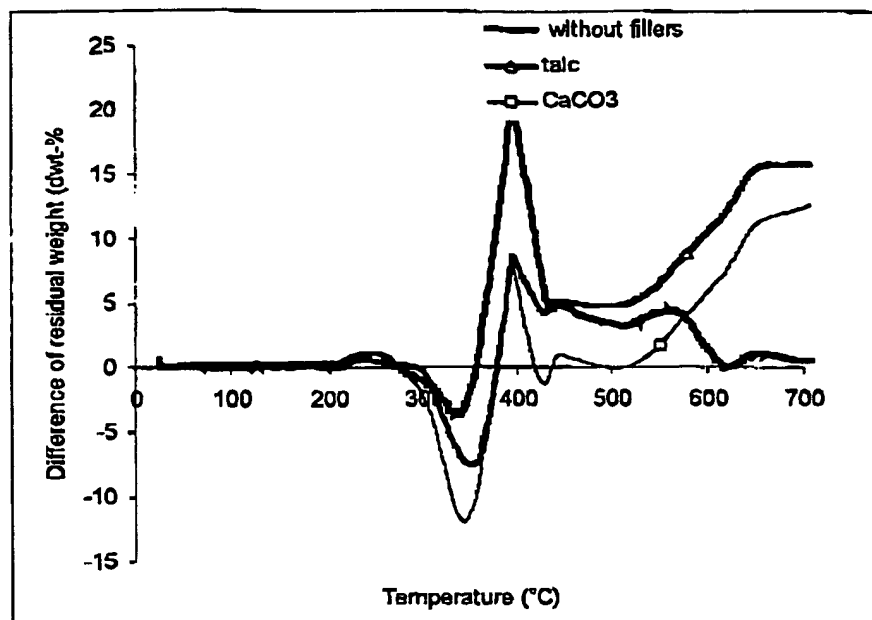
Fig. 8. Difference between experimental and theoretical TG curves of PP/PA-6/APP/EVA$_{24}$, PPtalc/PA-6/APP/EVA$_{24}$ and PPcarb/PA-6/APP/EVA$_{24}$ systems (under air flow).

In the case of PP/CaCO$_3$/PA-6/APP/EVA$_{24}$, the mass difference curve has the same shape as PP/PA-6/APP/EVA$_{24}$ up to 410°C which may be interpreted as above. Then the difference between experimental residual weight and computed residual weight is null until 560°C. There is no efficient shield which is formed as in the case of other blends. Over 560°C, the curve of mass difference increases.

The comparison between the curves of mass difference shows interesting results ; particularly over 560°C. The curves of filled systems with fillers increase whereas the curve of the blend decreases. This implies that interactions and reactions between polymer, and additives are larger with fillers. So, they may allow to form a structure which may block polymer links (or its degradation products) within the coating and therefore, to decrease the degradation rate of the system. These results are to be compared with the one observed in the case of APP/PER-Zeolite systems.[19]-[20] In these systems, zeolite is a synergistic agent which strongly enhances fire proofing performances. This acts by improving the "quality" of intumescent coating and by "trapping" polymer links (via the formation of stable aluminosilicophosphate esters) into the

structure which provides interesting mechanical properties to the shield. In our case, formations of calcium phosphate and magnesium phosphate are suspected.

Considering possible formation of magnesium phosphate and calcium phosphate, if only fillers and APP interact, the maximum residual weight is about 17 wt-% and 13.4 wt-% for talc and calcium carbonate. But, 32 wt-% and 28 wt-% with talc and calcium carbonate result from a thermo-oxidative degradation. This proves that a part of carbon is preserved at high temperature by the formation of a protective ceramic shield.

Another point could be pointed out. As observed by TGA, the use of $CaCO_3$ reduces the delay of stabilisation.
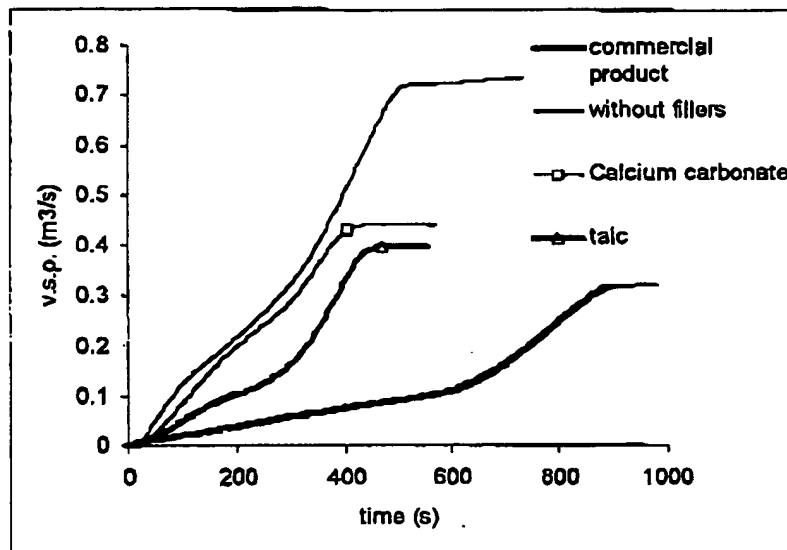
Fig. 9. Volume of Smoke Production (V.S.P.) emission versus time for PP/APP/PA6/EVA$_{24}$ formulations under an external heat flux of 50 kW/m^2.

Incorporating the fillers enable to reduce the amount of V.S.P. (Figure 9) increasing the conversion for a high temperature residue. Moreover, using talc enables to get a higher stability of the material which is maximal using the commercial product. Considering the amount of V.S.P. evolved without fillers, this is due to the combustion of a part of polymer.

Discussion

PP/APP/PA6/EVA$_{24}$ formulation presents enhanced fire performance in comparison with virgin PP. This improvement can be assigned to the formation of a carbonaceous shield during the combustion that slows down the degradation of formulations and that enables to form a stable residue.[12] With fillers, a similar behaviour is observed. The fire behaviour strongly depends on

the nature of fillers. It was first shown by Bertelli and al[21] that fillers, in particular hydrated silica or alumina decrease fire retardancy of PP based on intumescent systems with APP. Contrary to these results, Levchik and al[22] observed an increase in the fire properties with talc and calcium carbonate in PA-6/APP system.

Incorporating talc enables to get enhanced fire properties (decrease in the first RHR peak, increase of the residual weight). On the contrary, using calcium carbonate leads to a decrease in the fire performances. Moreover, a protective material does not form in the 420-520°C range and the residual weight obtained (31 wt-%) is lower than with talc (36 wt-%) whereas fillers were added in same quantities.

First, the results obtained with calcium carbonate could be explained by its basic properties. To obtain an intumescent behaviour, three ingredients are needed [12] : a carbonific or char former, an acidic species promoter and a « spumific » or gas-generating and inflating agent. The basic calcium carbonate reacts with APP to give calcium phosphate stable until 1400°C[23] and as a consequence forbids the formation of phosphoric acid and the intumescent char could not be formed as confirmed by visual observation during the cone calorimeter experiment. With $CaCO_3$, the samples do not blow up such as with talc or without fillers. The surface of the sample has the same colour at the end but, whereas with talc, the thickness of the sample increase from 3 mm to 15 mm in the middle whereas it is 3 mm for the burning sample with $CaCO_3$.

Many differences were observed when talc was added in our lab and with a commercial product. Many reasons could explain this phenomenon : first, the structure (cristallinity, cohesion of the blend)[1] strongly depends on the morphology and on the dimensions of the talc particles. As the composition of the intumescent blends are the same, the PP and talc characteristics are suspected to play a great part in the fire properties. Absence of information about the characteristic of the commercial PPtalc do not allow any discussion about this part.

Conclusion

This work shows the importance of the nature of fillers on the fire properties of an intumescent composite materials. In fact, whereas, it decreases with calcium carbonate, the fire behaviour is preserved or increased with talc. Moreover, the residual weight increases at the end because of the development of a ceramic at the surface To follow this work, an investigation on the blend composition would be undertaken after the process and after the burning of the sample.

To conclude the PPtalc/PA-6/APP/EVA$_{24}$ blend shows very good fire performance : LOI > 30 vol-%, R.H.R.$_{max}$ < 250 kW/m^2, a low level of CO, CO$_2$ and smoke emission which could allow to use it for some application.

Acknowledgement

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Optimization of a flame-retarded polypropylene composite

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Abstract

Composite materials demand constant improvements in mechanical and flame retardant (FR) properties. The goal of this project is to study the effect of additives on these properties in polypropylene composites containing glass fibers, pentabromobenzyl acrylate (PBBMA) as a primary FR and magnesium hydroxide as a secondary FR. Optimal composition is reached by means of statistical design of experiments (DOE) rather than by "trial and error" approach. The DOE approach allows minimization of the number of experiments, investigation of the influence of each additive and the mutual interactions between additives. It also allows here, prediction of optimal sample properties better than 8% from experimental values. The optimal composition exhibits improved mechanical and FR properties. Both FRs reduce the impact strength while enhancing flame retardancy. Glass fibers increase the modulus, but have only a moderate effect on the impact strength due to poor adhesion with PP. The interpretation of the effect of glass fibers on the flammability is inconclusive.
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Keywords: A. Glass fibers; A. Polymer-matrix composites; B. Mechanical properties; C. Statistics; Flame retardancy

1. Introduction

Polypropylene (PP) is a polymer of great importance in the industrial sector due to its low density, high water and chemical resistance, ease of processability and being one of the most cost-effective polymers available today. It is employed in numerous applications from non-woven fibers to the automotive industry. Its relatively low price is the driving force to improve its performance, to broaden its versatility and to enable it to compete with other polymers used nowadays for more demanding applications. PP as the polymer host requires the incorporation of additives and reinforcement in order to enhance its mechanical properties. One of the most commonly used reinforcement agents are chopped strand silane surface treated glass fibers. The glass fibers are surface modified since PP has a non-polar nature, which hinders its interaction and adhesion to polar fillers such as glass fibers. The surface treatment improves the compatibility of the glass with the PP

and hence improves the mechanical properties of the composite [1]. PP, in common with most synthetic polymers, is flammable and may therefore be hazardous near an open flame. It may also enhance fire propagation due to its tendency to drip when hot. Therefore, the addition of a flame retardant is an essential requirement if we wish to achieve a PP based composite with good flame resistance. Pentabromobenzylacrylate (PBBMA), used as a flame retardant in PP composites, is a crystalline monomer with a chemical structure shown in Fig. 1a. PBBMA may polymerize by free radical polymerization of the unsaturated acrylic bond initiated thermally during reactive extrusion to produce poly(pentabromobenzylacrylate) (PBBPA) [2] whose structure is shown in Fig. 1b. The fire retardancy mechanism of this FR and its suitability for use with PP has been discussed previously [3–5].

A fraction of PBBMA reacts to a variable degree [3] with PP to form either a graft (PP-g-PBBPA), or it may attach to low molecular weight PP chains as an end-group. The grafting of PBBMA onto PP may increase the polarity of the PP and thus enhance its adhesion to polar fillers, a role that is presently performed by modifiers such as maleic anhydride. More details can be

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(a)
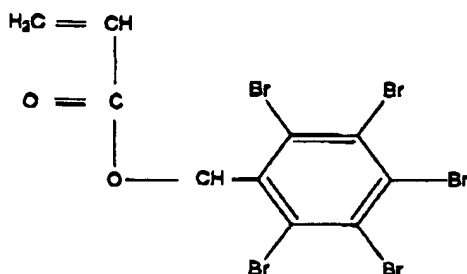
(b)
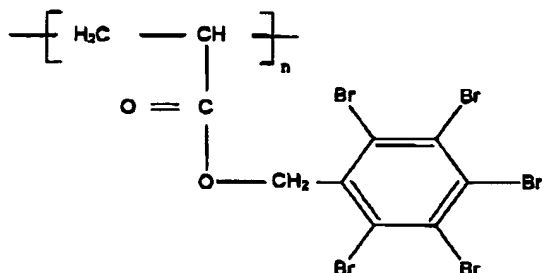
Fig. 1. Chemical structure of the FR: (a) monomer (PBBMA), (b) polymer (PBBPA).

found in our previous work [3–5] which dealt with the extent of thermal polymerization, grafting of the FR onto PP, and the amount of residual monomers left in the system. The influence of other additives on the reaction and resulting morphology was also reported in these references.

The addition of PBBMA imparts flame retardant properties to the PP composite and possibly improves its filler compatibility, as previously discussed. Yet, it also has adverse effects on the mechanical properties of the composite. Glass fibers may balance these antagonistic effects. Although added as reinforcement agent, glass fibers are also expected to improve flame retardant properties by diluting the host polymer. The addition of secondary additives may further improve or deteriorate the mechanical and flammability properties of the composite. Application requirements, which often demand different combinations of properties, may dictate the use of a specific composite material whose constituents will act synergistically to meet the needs of the application. The effect of each individual additive is easily determined by means of several simple experiments. How-

ever, synergistic/antagonistic interactions between the different additives are not obvious and require in-depth investigations. Usually, in designing a polymer possessing a specific set of properties, it is necessary to balance between the product costs and its properties, which should be at least equivalent if not better than those of the polymer host. There can never be a single ideal composite, since each additive contributes its own particular attributes. Thus, it is of practical importance first of all, to understand better the effect of different additives and the interactions between them in the most efficient way and secondly, to be able to forecast composite properties based on the knowledge acquired.

In this paper, we describe a method for the determination of the contribution of each of the additives (formulation variables) by means of the experimental design followed by statistical analysis of mechanical and flame retardant properties (responses). In this approach, the system is considered as a black box that is affected by a number of independent controllable input variables whose actions are transformed to the changes in the system responses. The variation of the measured response caused by the modification of controllable input variables can be translated to a predictive mathematical model. The model developed can then be used to predict response within the operating range of controllable variables.

In the next section the details of the experimental methods are described. The statistical methods used to design the experiments and analyze the data are detailed in Section 3. The effect of the different variables on the tested properties, their statistical significance, interactions between variables and the optimization of composite formulation are discussed in Section 4.

2. Experimental

2.1. Materials

The materials are all technical grade, commercially available and were used as received. A typical formulation was prepared by compounding the following materials:

Polymer matrix:
Polypropylene (3120MN1, Appryl, France) $d=0.9$ g/cm³, fusion temp = 163 °C.
Additives:
1. A. PBBMA (FR1025M, DSBG, Israel) primary FR;
   B. Antimony trioxide (ATO). A masterbatch of 80% Sb_2O_3 and 20% Low Density Poly(ethylene), characteristic diameter 1.5 µm (L0112 Kafrit, Israel) is added as FR synergist. For optimal FR activity, it is added in 1:3 ratio of ATO:PBBMA.

2. Irganox B225, a blend of Irganox 1010-hindered phenol type and Irgafos 168-phosphate type (Ciba Giegy, Germany). It is an antioxidant, which is added in order to prevent PP oxidation during compounding (the commercial PP above contains ~800 ppm of this antioxidant).

3. Magnesium Hydroxide, coated with 2% stearic acid (FR20, DSBG, Israel). It is used as multi-functional filler with intrinsic flame retardant properties. It serves as a secondary FR.

4. Chopped Glass Fibers with characteristic length 4.5 mm and characteristic diameter ~10 μm, $d=2.6$ g/cm^3 (P968, Vetrotex, France). Serves as the primary filler added in order to improve mechanical properties. The fiber surface is treated by the manufacturer with a silane-based coupling agent for better compatibility with PP.

5. Maleic Anhydride modified PP (PP-g-MAH). (Exxelor VM42E, Exxon Mobile, USA) $d=0.9$g/cm^3, used as a compatibilizer, gives the PP a somewhat polar nature. Only the grafted polymer is used, no free MAH is added to the composite.

In addition small amounts (0.2 wt.%) of Poly(ethylene) wax (AC-6A, Allied, USA) were added in order to reduce shear stresses developed during extrusion.

2.2. Compounding of composites

The five components listed above have been selected as *controllable input variables* for the optimization of the composite. The relative amounts of these additives and the way these amounts were selected will be described in the section dealing with the experimental statistical design. Once the amounts to be used had been determined, the composite was compounded as follows:

All formulations were compounded in a twin screw extruder (Berstorff ZE25 co-rotating, open vent, extruder $L/D=32$) at 250 °C, and 350 rad/min angular velocity of the screws rotation, and subsequently pelletized. The pellets were dried overnight, then injected by means of an Arburg Allrounder 320S injection molding machine into molds of the required specimen shape for the appropriate tests (e.g. 'dog-bone' shape for tensile test, rods for UL94V flammability test etc.). A nozzle temperature of 240 °C and an injection pressure of 1300 bar were employed.

2.3. Flame retardancy tests

2.3.1. Vertical UL94 (UL94V)
Rectangular rod shaped samples with dimensions of 127×12.7×3.2 (or 1.6) mm are exposed vertically to a methane gas burner flame for 10 s, as required by

UL94V. The sample is ignited at the bottom and burns upward. The time required for the flame to self extinguish after burner removal is measured and the occurrence of dripping onto a piece of cotton placed underneath the sample is recorded. The test is repeated for five different samples. If none of the samples burns for more then 10 s and the drips do not ignite the cotton, the material is classified as V-0. If none burns for more then 30 s and the drips do not ignite the cotton, the material is classified as V-1, but if the cotton is ignited the material classified as V-2. If any of the samples burns for more than 30 s or if the entire sample is consumed, the material is classified as non-rated (NR).

2.3.2. LOI (limiting oxygen index)
Samples shaped as rods or strips with dimensions 75×6.5×3 mm were enclosed in an open-vent chamber in a mixed oxygen/nitrogen environment. The sample is ignited at its upper end with a hydrogen flame. The sample burns from the top downwards. The atmosphere composition that permits steady burning is determined. The limiting oxygen index is the minimum fraction of oxygen in the gas mixture that will sustain burning for 3 min or 2 inches, (whichever comes first). The system was calibrated using a standard sample with a defined LOI value (ASTM D-2863-77). It should be reminded that it is incorrect to assume that material with an oxygen index over 21% can not burn in practice despite the fact air contains only 21% oxygen. Such an assumption disregards the fact that burning proceeds upward causing preheating so that materials with oxygen index over 21% will burn in air.

2.4. Mechanical tests

2.4.1. Izod impact reversed notched
The sample used here is the same as in UL94V test above. A standard notch (2.5 mm long and 0.25 mm notch tip radius) is applied to the specimen. For the reversed Izod, the notch is in the opposite direction to the striking hammer. The samples were examined in a Zwick apparatus. The striking energy of the pendulum was 1 J (ASTM D-256-81).

2.4.2. Tensile strength
The sample used in the tensile test has a 'dog-bone' shape in order for either necking or failure to occur in the center of the specimen and not near the clamps. The sample is loaded at a constant rate and the stress applied is recorded. The samples were tested in a Zwick 1435 apparatus. Measurement procedure and calibration was performed according to ASTM D-638-95. Before experiments were carried out optimal testing conditions were determined. It was determined that the tensile modulus for our samples should be obtained by

tests carried out in the range of extension forces between 200 and 600 N.

3. Statistical experimental design

3.1. Choice of the operating ranges for the controllable variables

The amounts of five additives were chosen as controllable input variables for the experimental design: glass fibers, PBBMA/ATO, PP-g-MAH, Irganox and $Mg(OH)_2$. The range of concentrations of each variable is shown in Table 1. The two FRs: PBBMA as a primary FR and $Mg(OH)_2$ as a secondary one, were selected for the following reasons. A flame-retarded PP composite based on Magnesium Hydroxide alone requires extreme FR loading up to 65% by weight, in order to achieve acceptable flame retardancy (V-0 classification). Such loading will result in a composite with very poor mechanical properties. The same is true for PBBMA, which requires a loading of approximately 30% if used alone [6]. The incorporation of both FRs in PP allows the use of lower amounts of FRs with better mechanical properties and at reduced cost, with identical flame retardancy properties.

The percentage of the PP itself has been set to a constant level of 38.5% in all formulations. Higher concentrations of PP in the composites result in unacceptable flame retardancy as can be seen in Table 2. These data show the narrow window available for PP concentration to obtain a formulation with acceptable flame retardant properties. For example, the sample containing 38.5% PP is classified as V-0. Increasing the PP concentration at the expense of $Mg(OH)_2$, by a mere 1.5% would result in improved mechanical properties but causes total flammability failure. The high sensitivity of flame retardancy to small changes in the matrix composition makes the use of statistical design an invaluable methodological approach. The 'best' composition obtained prior to the application of the statistical analysis serves as the starting point for the statistical analysis and will be referred to as the "best initial formulation".

On the basis of this narrow window, we attempt to optimize other components in the composite such that

Table 1
Constrains for controllable variables in DOE

Variable	Upper limit [+] (% w/w)	Lower limit [−] (% w/w)
Glass fibers	25	15
PBBMA+ATO (3:1)	20	13.3
MAH	2	1
Irganox	0.3	0
$Mg(OH)_2$	25	14.15

Table 2
Initial formulations

Component	Units	A1	A2	A3	A4
PP	%	38.5	40.0	42.0	44.0
Glass fibers	%	20.0	20.0	20.0	20.0
PBBMA	%	14.0	14.0	14.0	14.0
ATO	%	4.6	4.6	4.6	4.6
MAH	%	1.0	1.0	1.0	1.0
PE Wax	%	0.2	0.2	0.2	0.2
Irganox	%	0.3	0.3	0.3	0.3
$Mg(OH)_2$	%	21.4	19.9	17.9	15.9
UL-94 Rating (3.2 mm)		V0	NR[a]	NR[a]	NR[a]
Max. flaming time	s	10	19	55	50
Total flaming time	s	49	86	178	242
Cotton ignition		No	No	No	No
LOI	%	25.0-25.5	25.0-25.5	25.0-25.5	24.0-24.5

[a] NR, Non Rated in UL94 classification.

best possible mechanical and flame retardant properties are obtained. This implies that the amounts of these components in the composite are varied in a regular manner between maximum and minimum values based on prior knowledge.

1. The concentration of glass fibers was varied between 15 and 25% due to the superior mechanical properties achieved within these limits.
2. The primary FR PBBMA was used in combination with ATO as an FR synergist at an optimal constant ratio of 3:1 [7]. The selected upper limit for this FR (15%) is the value in the V-0 formulation in Table 2. Economical arguments set this as an upper bound for the FR. The lower limit (10%) is believed to be the lowest value that can still achieve V-0 flame retardancy in this system and even that only in the presence of other components.
3. The amount of PP-g-MAH is varied within the range from 1 to 2%. It is customary to add 2% of maleic anhydride to PP. The decision to use a smaller amount of PP-g-MAH as the lower limit was based on the assumption that PBBMA may also graft onto PP and play the same surface-modifying role as maleic anhydride.
4. The fourth variable is the antioxidant Irganox B225, which is a radical scavenger and may interfere with the polymerization of the PBBMA in the composite. Therefore the lower limit was set to zero and the upper limit was based on the amount customarily used in PP composites.
5. The amount of the last variable—the secondary FR ($Mg(OH)_2$), was set by the overall amount of the other components to add up to 100%.

3.2. Statistical methods

The optimization of the formulation compositions with respect to their desirable characteristics (called *responses*) is performed using the technique of mixture design. The outcome of the experimental design is a mathematical expression for the value of the responses as a function of the different ingredients in the composite (named *factors*). The total number of experimental points is the smallest number of experiments that still enable the formulation of this mathematical expression which is termed the *response surface* and can be represented by the following quadratic regression formula [8]:

$$R = \sum_{i=1}^{q} b_i x_i + \Sigma \sum_{i<j}^{q} b_{ij} x_i x_j$$

where R, the experimentally measured response; x_i, concentration of the ith ingredient (the values of x_i are prescribed by the statistical design and are known for each experimental plan); b_i, the regression coefficients, values of which are chosen to achieve the best fitting of the model to the given experimental data; and q, the number of ingredients in the mixture.

The terms of the type $b_i x_i$ express the direct influence of the ith ingredient on a certain response R ("*main effects*" of factors): the higher the value of b_i, the greater the influence of the ingredient on the response. The terms of the type $b_{ij} x_i x_j$ express the so-called *interactions* between factors. These interaction terms reflect the non-additivity in the influence of pairs of factors on a given response: the higher the value of b_{ij}, the higher the degree of non-additivity in the combined influence of the ith and jth factors on the response.

The statistical significance of the factor effects is obtained by comparison of the b_i values with the estimate of the random noise in the system. This estimate is obtained as the standard deviation in a series of repeated experiments built into the experimental plan. The *main effects* are estimated by the approximate t-test in the framework of the mixture linear model. The *second order interactions* between variables are estimated by a t-test in the framework of a mixture quadratic model. The level of significance for all statistical tests, both for the main effects and second order interactions, was chosen to be $\alpha = 0.05$. In other words, if a p-value in a test for the significance of a certain *factor* is smaller than 0.05, this factor is considered statistically significant at $\alpha = 0.05$ level of significance. One should remember, that the p-value represents the smallest level of significance that would lead to rejection of the null-hypothesis (i.e. there is no effect of the controllable factor on the response under investigation) while this hypothesis is true. The smaller the p-value obtained in the analysis of the influence of a certain factor on the response under investigation, the higher the probability that this factor

does influence the response. Factor interactions of third or higher orders are assumed to be negligible, as is routinely practiced in the DOE process.

The design of experiments of choice was a two-level plan, i.e. the concentration of each factor (ingredient) was examined at two levels, the high and the low levels of concentration. Specifically, the experimental plan was a D-optimal two-level mixture design for five variables. The statistical analysis of the chosen D-optimal mixture design was performed by "Design Expert" software [Design-Expert[nc] V 5.0.8, Stat-Ease-Corp., Minneapolis MN 55413-9827 USA].

The *control factors* (i.e. concentrations of the additives) and their experimental *constraints* (high [+] and low [−] levels) are presented in Table 1.

The experimental matrix included 20 runs: 15 runs for the quadratic model, 2 runs for the curvature estimation and 3 replicate runs for the estimation of the random noise [9]. The experimental plan was created and analyzed by the "Design Expert" software. The full experimental matrix is presented in Table 3. The experiments were performed in a completely randomized sequence as set by the software. The final outcome of the analysis is an optimal composition with its associated desirability value (1.0—highly desirable, 0—highly undesirable) and predicted properties.

4. Results and discussion

The results of all the mechanical and flame retardancy tests performed are listed in Tables 4 and 5.

4.1. Statistical analysis of the factors and the interactions on the mechanical properties

In general, the statistical analysis demonstrates the existence of statistically significant effects, both "main effects" and "interactions". The following paragraphs present the results of the statistical analysis of the chosen D-optimal mixture design and the discussion of influence of main effects and of interactions on the composite properties.

4.1.1. Modulus

Only PP-g-MAH has a statistically significant influence (p-value = 0.01) on the composite modulus at the main-effect level of analysis. Maleic anhydride is primarily used as a modifier in order to improve the adhesion between the polymer host and the glass fibers by facilitating the interaction between the non-polar PP and polar filler. Such interactions are known to increase the modulus of PP composite [10]. On the other hand, PP-g-MAH is known to adversely affect the modulus of bulk PP by hindering PP crystallization [11]. Under normal circumstances the improved adhesion overcomes the

Table 3
Experimental matrix for the mixture design

Component	Units	1	2	3	4	5	6	7	8	9	10
		Formulation No.									
PP	%	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50
Fibers	%	25.00	21.68	25.00	17.78	15.00	25.00	15.00	23.35	15.00	22.85
PBBMA	%	10.00	12.50	12.50	13.90	14.63	15.00	14.74	10.00	14.74	10.00
ATO	%	3.30	4.15	4.15	4.64	4.87	5.00	4.91	3.30	4.91	3.30
MAH	%	1.50	1.00	1.00	1.77	2.00	1.50	2.00	1.00	2.00	2.00
PE Wax	%	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Irganox	%	0	0.30	0.15	0.22	0.30	0	0	0.30	0	0.30
Mg(OH)2	%	21.50	21.67	18.50	22.98	24.50	14.80	24.65	23.35	24.65	22.85

	Units	11	12	13	14	15	16	17	18	19	20
PP	%	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50	38.50
Fibers	%	20.00	20.85	25.00	18.65	25.00	18.10	25.00	15.15	20.00	22.85
PBBMA	%	15.00	10.00	12.50	12.50	15.00	12.30	15.00	15.00	15.00	10.00
ATO	%	5.00	3.30	4.15	4.15	5.00	4.10	5.00	5.00	5.00	3.30
MAH	%	1.00	2.00	2.00	1.00	1.50	1.50	1.50	1.00	2.00	2.00
PE Wax	%	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Irganox	%	0.30	0.15	0	0	0.30	0.30	0.30	0.15	0.15	0.30
Mg(OH)2	%	20.00	25.00	17.65	25.00	14.50	25.00	14.50	25.00	19.15	22.85

Table 4
Flame retardancy results of the mixture design matrix

	Units	1	2	3	4	5	6	7	8	9	10
		Formulation No.									
UL-94 Rating (3.2 mm)		VI	VO	VI	VO	VI	VO	VO	NR[a]	VO	NR[a]
Max. flaming time	s	26	9	19	6	23	2	0	48	0	32
Total flaming time	s	143	27	83	9	64	4	0	182	0	120
Cotton ignition		No	No	No	No	No	No	No	Yes	No	No
UL-94 Rating (1.6 mm)		NR[a]	VI	NR[a]	VO	V2	VO	VO	NR[b]	VO	NR[a]
Max. flaming time	s	32	19	40	5	26	4	5	55	5	39
Total flaming time	s	227	71	142	25	85	12	13	266	15	161
Cotton ignition		Yes	No	Yes	No	Yes	No	No	Yes	No	Yes
LOI	%	24.0–24.5	25.5–26.0	25.0–25.5	26.0–26.5	26.5–27.0	25.0–25.5	26.0–26.5	24.5–25.0	25.0–25.5	24.5–25.0

	Units	11	12	13	14	15	16	17	18	19	20
UL-94 Rating (3.2mm)		VO	NR[a]	VI	VO	VI	VI	VI	VO	VO	NR[a]
Max. flaming time	s	7	40	13	1	13	12	24	4	10	60
Total flaming time	s	30	134	41	1	44	42	65	6	45	257
Cotton ignition		No	No	No	No	No	No	No	No	No	Yes
UL-94 Rating (1.6mm)		VO	NR[a]	V2	VO	VI	NR[a]	NR[a]	VO	VI	NR[a]
Max. flaming time	s	9	53	20	2	19	47	31	3	10	45
Total flaming time	s	48	241	100	5	102	128	86	8	54	222
Cotton ignition		No	Yes	Yes	No	No	No	No	No	No	Yes
LOI	%	25.5–26.0	24.0–24.5	24.0–24.5	25.5–26.0	25.0–25.5	25.0–25.5	25.5–26.0	26.0–26.5	26.0–26.5	24.0–24.5

* NR, Non Rated in UL94 classification.

negative effect on crystallization resulting in overall increase in modulus. Contrary to our expectations, a higher maleic anhydride concentration resulted here in a lower composite modulus. A possible interpretation is as follows: the FR replaces PP-g-MAH at the fiber surface hence reducing the effectiveness of PP-fiber interaction. As a result, we hypothesize that in the present formulation the maleic anhydride favors the PP bulk on the PP-glass fibers interface. In the PP bulk the grafted MAH groups of the PP-g-MAH interfere with PP crystallization. This interpretation is not supported by any direct experimental observation but is indirectly inferred from DSC measurements, which show that maleic anhydride lowers the amount of crystalline PP [3]. The heat of fusion measured by DSC reflects the degree of crystallinity of a composite. When the heats of fusion

Table 5
Mechanical properties results of the mixture design matrix

	Units	1	2	3	4	5	6	7	8	9	10
	Formulation No.										
Modulus	MPa	6297	6288	6488	4777	4874	6521	4508	6396	4245	5690
Max. strength	MPa	39.2	40.9	41.7	37.6	37.9	42.3	36.4	41.5	36.2	39.6
Impact	J/m	78.7	87.8	101.5	100.0	103.4	98.7	90.6	97.5	89.4	90.3
σ	J/m	2.4	5.4	2.5	8.9	2.8	4.2	9.1	8.4	2.8	6.8
	Units	11	12	13	14	15	16	17	18	19	20
Modulus	MPa	5683	5373	5803	5082	6032	4890	6021	4354	5047	5444
Max. Strength	MPa	40.4	37.6	39.7	36.6	40.4	36.7	40.3	36.7	38.2	39.1
Impact	J/m	95.0	92.5	82.2	83.7	101.2	93.1	93.1	95.6	85.6	96.9
σ	J/m	7.2	10.2	5.9	5.6	10.0	4.6	4.6	6.5	5.2	4.4

and crystallization were analyzed as responses in the framework of DOE, an increase in maleic anhydride concentration was shown to decrease the heat of fusion and even more significantly, the heat of crystallization (p-value = 0.06).

4.1.2. Maximal strength

At the main-effect level of analysis we find again that the addition of maleic anhydride (in the form of PP-g-MAH) lowers the mechanical properties of the composite, in this case the maximal strength (p-value = 0.02). This is ascribed, as before, to the lowering of PP crystallinity.

In addition to the main-effect we also find here substantial negative interactions of second order:

1. Glass fibers enhance maximal strength at low concentrations of maleic anhydride in a more pronounced way than at high concentrations (p-value = 0.05).

2. The addition of large amounts of PBBMA over the entire range of PP-g-MAH concentrations results in decreased values of maximal strength relative to those observed with low amounts of PBBMA (p-value = 0.06).

3. The addition of PP-g-MAH in presence of Mg(OH)₂ results in lower maximal strength (p-value = 0.08).

All of the above indicate a poor modifying effect of maleic anhydride in the presence of the FR apparently due to its reduced role in adhesion at the polymer–filler interface. Maleic anhydride may interact with filler surfaces via a reaction between its functional group and OH groups on Mg(OH)₂ or glass fibers [10]. PBBMA may also react with the fillers via a radical mechanism and hence compete with the maleic anhydride for sites on the surface of those fillers. This may force the maleic anhydride away from the filler surface and into the bulk of the PP matrix. It may be concluded that since both the glass fibers and the Mg(OH)₂ are surface modified to render them less polar, the addition of the

maleic anhydride (PP-g-MAH) as compatibilizer was unnecessary in this case and had negative effects as result of rejection by the other additives.

4.1.3. Izod impact

Statistical analysis of factor-influences on impact strength, as determined by the notched Izod Impact test, failed to reveal any significant effects. This was due to, the large scatter in the data (the range of measured values was 15 (a.u.) with an absolute standard deviation of ~8) that may have masked any effects present.

Statistical analysis of the reversed notched Izod Impact test results showed that all of the factors under investigation had significant influence as main effects on this response. There were no statistically significant interactions.

Increasing the PBBMA concentration causes a reduction in impact strength (p-value = 0.04). We have determined [3,4] that in its monomeric form the FR is insoluble in the matrix, while in its polymeric form it modifies the morphology of PP. It is difficult at this point to determine the exact mechanism by which the FR reduces the impact strength of the composite. Yet, it may be attributed either to the change in morphology, to a plasticizing effect of the monomeric FR, to a change in interaction between adjacent PP chains due to FR grafting, or to a combination of these effects.

Increasing the concentration of Mg(OH)₂ particles also affects adversely (p-value = 0.02) the impact strength. The presence of high loading of solid particles embedded in the polymer matrix results in reduced ability to absorb impact energy. This is due to the filler effect, which damages matrix continuity, and each particle is a site of stress concentration, which can act as a microcrack initiator [12]. Mg(OH)₂ is sized with stearic acid, which comprises a long carbon chain that adheres to the polymer matrix. It may be argued that these chains reduce stress concentration in the particle vicinity, but apparently its effect is insufficient to overcome the negative effect of the high loading of particles. Thus, the net result is a decrease in impact strength.

The addition of maleated PP also reduces composite impact strength (p-value = 0.07). This may be attributed, as before, to its effect on the morphology and chain conformation in the PP matrix.

Glass fibers have the most unexpected effect observed in the reduction of impact strength within the 15–25% loading range (p-value = 0.02). The increase of glass fiber concentration from low level to high level causes a small, but statistically significant decrease (i.e. gentle negative slope) in impact strength. This is in contrast to the large expected increase in impact strength and the increase observed in PP composite, which contain only glass fibers. Glass fibers are presumed to disperse the impact energy over a large volume, especially when the fibers are surface treated with silane coupling agents to improve direct interaction with the PP matrix. In addition, glass fibers have the role of fracture propagation inhibitors [13]. We have shown [4] that in this composite, despite the sizing, there is poor adhesion and therefore the glass fibers act as an additional solid filler with a detrimental effect on composite impact resistance, as discussed above.

Increasing the Irganox B225 concentration increases the impact strength (p-value = 0.02). This may be attributed to the prevention of PP oxidation. PP oxidation gives rise to end products such as ketones, which in turn may lead to chain degradation and reduction in molecular weight resulting in loss of mechanical properties. In addition, Irganox, as a radical scavenger, should inhibit secondary undesirable reactions of free radicals formed during a mechanical fracture of the chains.

4.2. Statistical analysis of the factors and the interactions on the flame retardant properties

Prior to the discussion of flame retardant properties, we will briefly review the flammability tests carried out.

For a given product, the fire hazards in different areas of application (e.g. building, transportation, electrical consumer products, textile etc.) are so different that flammability information from one category, does not apply to another. Even within one category there is large variability between specific applications. Standard laboratory tests try to remove unimportant parameters in a certain situation and focus on the relatively important ones. However, these tests do not predict material behavior in actual fire, because they are limited to small laboratory scale fire simulations. These tests are intended only to compare between flammability properties of different materials under similar fire conditions. One cannot compare results obtained by different tests because of lack of correlation due to the different purpose and the different fire situation partially reproduced in each test. These flammability tests also differ in different countries based on local regulations and standards. In our particular case, the two tests employed are classified

as combustibility tests. The LOI test which is common for materials used in coverings and linings, and in cables and wires for the construction industry, expresses flammability performance by a numerical value—the oxygen index (cf. Section 2). UL94V is commonly used in applications other than building materials, especially in the electrical consumer products industry (plastic parts in devices and appliances). UL94V classifies a product by its flammability based on a qualitative scale [14]. PP the polymer used here, is classified as NR in UL94V and has a LOI value of 17–17.5.

In the evaluation of UL94V results, only the total flaming time was subjected to statistical analysis. As explained in the Experimental section above, each test is repeated for five different samples of the same composition. The flaming time results for V-0 class samples are relatively reproducible with low dispersion (for example in case of a 3.2 mm thick sample the typical flaming time is $\tau \sim 1$ s with standard deviation of $\sigma \sim 1.6$ s). As classification deteriorates the results are prone to be more erratic with higher dispersion of flaming times (V-1: $\tau \sim 10$ s, $\sigma \sim 4.5$, s; NR: $\tau \sim 26$ s, $\sigma \sim 14$ s). Therefore, in order to reduce variability and scatter in the results, we have chosen the total flaming time which is considerably more reproducible, as the response for the statistical analysis rather than other measures such as the maximal flaming time.

The UL94V measurement was performed on samples of 3.2 and 1.6 mm thickness. Although test results may differ between samples of different thickness, the results of the statistical analyses yield identical effect of all input variables on the flammability irrespective of thickness.

Statistical analysis of LOI indicates that variations of PBBMA and $Mg(OH)_2$ concentrations within the selected ranges have no statistically significant effect. This is most surprising. In contrast, UL94V statistical evaluation of the FRs shows that increasing the PBBMA concentration has the most significant effect in lowering the total flaming time (p-value = 0.003). This implies a superior flame retardant property, as expected. Increasing the $Mg(OH)_2$ concentration also reduces the total flaming time, as would be expected from a secondary flame retardant (p-value = 0.05). The expected effect of both FRs on the flammability of the samples as determined by the UL94V test is in contradiction to the lack of any significant effect measured by the LOI test. It implies that the LOI test is not sensitive enough to differentiate between the flammability levels of the compositions tested here.

Statistical evaluation of the LOI shows that increasing Irganox B225 concentration increases slightly the LOI (p-value = 0.09). Whereas, UL94V evaluation shows that increasing Irganox concentration results in higher total flaming time (p-value ≈ 0.04). The higher flaming time may be attributed to the role of Irganox as an

inhibitor of the PBBMA radical polymerization. PBBPA, which is formed in situ during extrusion, is well dispersed in the PP matrix whereas the PBBMA is undissolved in the PP matrix [4]. The homogeneous dispersion of the PBBPA in the matrix allows for better Br release and therefore better flame retardancy. Irganox may inhibit the PBBMA radical polymerization and hence increase total flaming time. In addition, the high extent of polymerization caused by the low concentration of Irganox, may increase the viscosity of the composite and subsequently, decrease the flowability during UL94V test. In view of the larger p-value obtained in the LOI statistical analysis, the conflicting result from the UL94V experiment and the smaller sensitivity of LOI test we consider the increased FR property obtained by the latter as questionable.

Increasing the PP-g-maleic anhydride concentration results in a lower LOI (p-value = 0.03). No statistically significant effect was found in UL94V. This effect is due to the higher chemical activity of PP-g-MAH and lower molecular weight PP-g-MAH chains, which have high decomposition rate.

Increasing the glass fibers concentration lowers to some extent the total flaming time (p-value = 0.1). In contrast, increasing the glass fiber concentration lowers the LOI (p-value = 0.08). Decreased total flaming time is attributed to a straightforward dilution effect of the polymer matrix by the glass fibers. By the same reasoning, we would also expect an increase in LOI, contrary to our experimental findings. In the following we shall try to explain this surprising effect. One possible mechanism for enhanced flammability is based on the substantially different thermal expansion coefficients of glass-fibers and the PP matrix. Upon cooling of the composite after the compounding, unequal contraction leads to a "tunnel effect" that may cause the formation of air pockets around the glass fibers. The air trapped between the glass fibers and the polymer matrix will not only enhance the burning, but also contribute to the poor adhesion between the glass and the PP implied in the discussion of mechanical properties above. The proposed mechanism does not address the question of polymer creep into the air pockets eliminating eventually their existence. Further experimentation is required to test this hypothesis.

It is observed that the two flammability tests (LOI and UL94V) result in a contradiction as to the effects of glass fibers. This contradiction may be ascribed to the different nature of these tests [15]. Brominated flame retardants work by releasing HBr gas into the flame where it acts as a free radical scavenger. In order to quench the free radical chain reactions that constitute the burning process, the HBr has to achieve critical minimum concentration. The chimney-like construction of the LOI apparatus and the continual gas flow prevent the HBr from reaching this critical concentration. On the other hand, the relatively static atmosphere around the burning UL94V sample allows this critical HBr concentration to be achieved. This is the source of difference between the two test methods.

The other possible explanation for increased flammability in LOI and decreased flammability in UL94V is based on the order of magnitude higher thermal conductivity and thermal diffusivity of the glass fibers relative to the PP matrix. Using this argument, the glass-fibers play the role of heat conductors. They conduct the heat faster into the composite and thereby contributing to further PP decomposition and release of combustible gases. This progressive breakdown also results in bromine release. Since as explained earlier, the LOI is performed in a continuously rejuvenated environment due to oxygen flow, the bromine atoms in the gas phase are being continually withdrawn from the flaming area, thus preventing them from reaching that critical concentration, which would quench the free radical reactions. The UL94V is performed in a stagnant environment where the bromine atoms are able to perform their function, and the opposite statistical influence is observed.

Finally, glass fibers have a large effect on UL94V test results by the imparted increase in the viscosity of the heated composite. By reducing the flowability of the composite, an anti-dripping effect is achieved, which leads to better UL94V evaluation. Dripping and flowability are also affected by the thickness of the sample.

There was no indication of second order interactions in the LOI statistical analysis. The UL94V statistical analysis revealed several mutual interactions. The interaction between PBBMA and glass fibers is significant (p-value = 0.04): the combination of a high level concentration of PBBMA with a low level concentration of glass fibers causes a significant decrease in total flaming time. The interaction between PBBMA and Mg(OH)$_2$ is also significant (p-value = 0.05): again the combination of high concentration of PBBMA with low concentration of Mg(OH)$_2$ causes a significant decrease in total flaming time. This is a somewhat puzzling result since one would expect that the higher the total amount of FRs (primary and secondary) the lower would be the flaming time since there is no evidence for adverse effect of one FR on the other. Thus, the results from the statistical analysis may hint at an indirect effect (e.g. increased melt viscosity, reduced polymerization of PBBMA etc.), which is responsible for the negative interaction parameter obtained from the statistical analysis. We are unable to offer an explanation for this result at this point.

4.2.1. Search for optimal composition

On the basis of the statistical analysis presented above, we tried to construct the optimal composition of the PP formulation. The most crucial step in the optimization process is the ranking of the composite properties by

their importance. The basic concept of optimization means compromise in some values in order to reach higher values in others. The properties with respect to which this optimization was performed were chosen as maximal *reversed notched* impact strength (representative mechanical property) and minimal total flaming time, which provides V-0 in UL94V test (representative flame retardant property).

After conducting all 20 experiments of the D-optimal mixture design, the software constructs an algebraic equation (statistical model), which connects the measured responses with the values of factors under investigation. This statistical model can be employed for searching the optimal conditions, once the most important responses are specified. The optimization procedure performed by the software yielded three formulations, which were expected to meet the optimization requirements. The predicted optimal formulations are presented in Table 6, together with the experimentally measured responses for these 'optimal' formulations. The main feature of these results is the similarity of these proposed compositions as well as the measured characteristics of these formulations. To appreciate the predictive power of the statistical model, we have compared the predicted characteristics of the best-proposed formulation (desireability = 0.995; Table 6 sample B1) with experimentally obtained characteristics. The results of this comparison are presented in Table 7. All predicted responses, with the exception of the modulus, are in

extremely good agreement with the experimentally obtained values. The confidence limits of the predicted values for the responses do not exceed 8% (see Table 7). Specifically, the confidence limits for the impact, maximal strength and LOI are equal to ±8, ±4.8 and ±2%, respectively. In contrast, the experimental modulus was markedly higher than that predicted by the model. We are unable to explain this discrepancy.

Table 8 presents the characteristics of four formulations: the *"best initial formulation"* (A1), the best predicted formulation by the DOE model (B1) and additional two formulations found in the course of DOE study which seem to have highly desirable properties. The two latter samples have been added to ascertain that the formulation chosen by the statistical procedure as *optimal formulation* is indeed the best available. One may observe that the best formulation predicted by the statistical model is a desirable compromise between mechanical and flammability characteristics: relatively

Table 6
'Optimal' formulations and test results

Component	Formulation No.			
	Units	B1	B2	B3
PP	%	38.50	38.50	38.50
Fibers	%	22.31	24.10	24.77
PBBMA	%	15.00	15.00	15.00
ATO	%	5.00	5.00	5.00
MAH	%	1.00	1.30	1.41
PE Wax	%	0.20	0.20	0.20
Irganox	%	0	0	0
Mg(OH)₂	%	17.99	15.90	15.12
UL-94 Rating (3.2mm)		V0	V0	V0
Max. flaming time	s	0	1	1
Total flaming time	s	0	1	2
Cotton ignition		No	No	No
UL-94 Rating (1.6mm)		V0	V0	V0
Max. flaming time	s	1	2	2
Total flaming time	s	6	4	3
Cotton ignition		No	No	No
LOI	%	25.5–26.0	25.5–26.0	25.0–25.5
Modulus	MPa	6953	6834	7203
Max. strength	MPa	41.8	42.1	41.6
Impact	J/m	90.6	91.9	89.4
σ	J/m	3.8	4.7	5.7

Table 7
Comparison between model prediction and experimental results of formulation B1

Response	Predicted results		Experimental results	
	Mean	A 95% confidence interval	Experimental value	A 95% confidence interval
Modulus	5908	5578–6237	6953 (av.)	6470–7436
Impact	90.0	82.7–97.2	90.6 (av.)	87–94.2
Max. strength	42.3	40.3–44.4	41.8 (av.)	40.9–42.8
Total flaming time (1.6 mm)	7	(–48)ᵃ–55	6	–
Total flaming time (3.2 mm)	(–22)ᵃ	(–68)ᵃ–25	0	–
LOI	25.4	24.9–25.9	25.5 - 26	–

ᵃ Physically equivalent to value of zero.

Table 8
Properties of the optimal formulations

	Initial formulation	The DOE optimal formulations		
	A1	The best predicted	The best formulations in the DOE experimental matrix	
		B1	6	4
Impact	103±3	90±4	99±4	100-9
Modulus	6333	6953	6521	4777
UL94 (1.6 mm)	T= 109 V1	T=6 V0	T= 12 V0	T=25 V0
UL94 (3.2 mm)	T=49 V0	T=0 V0	T=4 V0	T=9 V0
LOI (%)	25.0–25.5	25.5–26.0	25.0–25.5	26.0–26.5

high impact and V-0 rating (i.e. low total flaming time). The comparison of the latter formulation with the initial formulation demonstrates the compromise character of the process optimization: by accepting a slight decrease in impact value a dramatic improvement in flame retardancy is obtained. It is instructive to examine in detail the two additional compositions selected as superior formulations. Both of them are found to be inferior to (B1) the best predicted formulation. Total flaming time (1.6 mm) in these formulations is 12 and 25 s, respectively, as opposed to 6 s for the optimal formulation. However, if we take into account the high value of the standard error of the predicted mean for this response (22 s), we are obliged to reject these formulations, since the total flaming time in UL94V = (V-0) is not allowed to exceed 50 s. Indeed, these two formulations fail the UL94V test regarding V-0 at the $\alpha = 0.05$ confidence level, if we take the total flaming time as a sum of the predicted mean (12 or 25 s) and twice the standard error ($22 \times 2 = 44$ s).

5. Conclusions

The technique of statistical experimental design has been employed to obtain an optimal formulation of high loading polypropylene composite with suitable mechanical and flame retardancy properties. The DOE technique helps optimize a set of flame retardant additives, which guarantee acceptable flame retardant properties with minimal negative effect on mechanical properties. Moreover, it allows the study of the influence of individual additives and the mutual interactions in the composite within the chosen concentration working range. DOE provides a route to obtain the optimal formulations, and to get the abovementioned information with the minimum number of experiments.

An optimization of different additive loads was performed and the final polypropylene composite exhibited improved mechanical and flame retardant properties. The DOE scheme allows a prediction of most sample properties within 8% from the actual experimental values. In a typical PP composite under investigation, we observed that maleic anhydride lowers the modulus and impact strength. This was attributed to the failure of maleic anhydride to enhance adhesion at the interface between PP and the different fillers and its effect was reduced to a plastizing effect in the bulk. As expected, PBBMA and $Mg(OH)_2$ decrease the composite impact strength and enhance flame retardant properties. Glass fibers increase the modulus as a reinforcing agent, but have only a moderate effect on impact strength within the investigated range, probably due to poor adhesion with PP. Contradictory results have been obtained for the effect of glass fibers on flame retardant properties. Different explanations for these results have been suggested, but no definitive conclusion is possible at this point.

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